

09/601015

534 Rec'd PCT/PTC 24 JUL 2000

THREE DIMENSIONAL OPTICAL MEMORY  
WITH FLUORESCENT PHOTSENSITIVE MATERIAL

BACKGROUND OF THE INVENTION

The present invention relates to a high-  
5 quality, high-density, three-dimensional optical  
memory, and more particularly to a method and apparatus  
for the storage and retrieval of digital data on a  
three-dimensional optical memory.

Optical data storage is a known form of data  
10 storage. Known optical storage media such as compact  
disks, CD-ROMs, and DVDs are two-dimensional media  
storing separate bits of information in separate small  
areas on one or more surfaces. Although these optical  
data storage media have the capacity to store large  
15 amounts of information, there is an ever-increasing  
need to increase capacity and improve access time  
because computer applications are continually growing  
in size. However, there are physical limits as to how  
small the areas for storing information can be, as  
20 such, these memories are reaching theoretical limits in  
storage capacity. In addition, access time is  
deteriorating as storage capacity increases. It is  
also desired that such computer memories have low-cost,  
small size and low energy consumption.

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A solution to the desire for increased storage capacity, fast data transfer, and improved access time is the use of the third dimension in optical storage memories. Known three-dimensional optical storage memories have data storage densities that exceed the storage capacity of any present conventional two-dimensional optical storage memories (such as CD-ROMs) by more than three to four orders of magnitude. The increase in storage capacity stems from the ability to store information in any volume of a three-dimensional memory.

For example, the maximum theoretical storage density for a two-dimensional optical disk is  $1/\lambda^2 = 3.5 \times 10^8$  bits/cm<sup>2</sup>, while the storage density for a three-dimensional memory is  $1/\lambda^3 = 6.5 \times 10^{12}$  bits/cm<sup>3</sup>, assuming that the same wavelength of light  $\lambda = 532$  nm is used to access the information.

Another form of high capacity optical storage medium is a three-dimensional holographic memory. Three-dimensional holographic memories also have data storage densities that exceed the storage capacity of known two-dimensional optical storage media. Experiments have been conducted on three-dimensional data storage using holographic memories made of photo-refractive materials (see D. Psaltis and F. Mok, Scientific American, November 1995, p. 52).

Although known three-dimensional memories provide improvements (e.g., access speed and storage capacity) over known two-dimensional storage memories, even these memories eventually will reach a limit in storage capacity unless a storage and retrieval process is developed which can better utilize every available volume in a three-dimensional storage memory.

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Accordingly, it would be desirable to provide a data storage and retrieval system that increases the storage capacity of three-dimensional optical memories.

It would further be desirable to provide a  
5 three-dimensional optical memory that has an increased storage capacity over known optical memories.

#### SUMMARY OF THE INVENTION

It is an object of this invention to provide a data storage and retrieval system that increases the  
10 storage capacity of three-dimensional optical memories.

It is another object of this invention to provide a three-dimensional optical memory that has an increased storage capacity over known optical memories.

In accordance with the present invention,  
15 there is provided a three-dimensional optical memory made from a fluorescent photosensitive material, as well as a method and apparatus for storing and retrieving data on such a three-dimensional optical memory. Writing and reading of information on the  
20 optical memory is carried out with a coherent light source in conjunction with a confocal microscope. The confocal microscope is used to select a specific very small volume in the three-dimensional fluorescent photosensitive optical memory. The selected volume of  
25 fluorescent photosensitive memory is written by being irradiated (e.g., by a laser) at a wavelength that causes a transition producing either a fluorescence extinction or a fluorescence enhancement in the optical memory material. The memory is read by exciting at  
30 least the volume to be read at the fluorescence excitation wavelength of the memory. The presence or absence of fluorescence, caused by either fluorescence

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extinction or enhancement, can be used to represent 0's and 1's.

The storage and retrieval system of the present invention also preferably uses a two-photon absorption process to localize volumes in a three-dimensional medium. Two-photon absorption allows for writing to individually selected volumes of the optical memory without affecting neighboring bit locations, which allows smaller volumes to be used for each bit location, thus increasing memory capacity.

A two-photon absorption process involves the excitation of a molecule to an electronic state of higher energy by the absorption of two photons. A first photon emitted by a first excitation beam at a first predetermined wavelength excites the molecule to a virtual state, while a second photon emitted by a second excitation beam at a second predetermined wavelength further excites the molecule to a real excited state. The wavelengths of the two excitation beams are such that although neither beam is absorbed individually, the combination of the two wavelengths is in resonance with a molecular transition of the memory material.

Examples of fluorescent photosensitive materials that can be used for the three-dimensional optical memory of this invention are fluorescent photosensitive glass and fluorescent photosensitive vitroc ceramic. Both of these materials have the ability to fluoresce but are also photosensitive, changing their ability to fluoresce in response to applied radiation.

#### BRIEF DESCRIPTION OF THE DRAWINGS

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The above and other objects and advantages of the invention will become apparent upon consideration of the following detailed description, taken in conjunction with the accompanying drawings, in which  
5 like reference characters refer to like parts throughout, and in which:

FIG. 1 is a diagrammatic representation of a first preferred embodiment of a writing configuration of the data storage and retrieval system according to  
10 the invention;

FIG. 2 is a diagrammatic representation of a second preferred embodiment of a writing configuration of the data storage and retrieval system according to the invention;

15 FIG. 3 is a diagrammatic representation of a first preferred embodiment of a reading configuration of the data storage and retrieval system according to the invention;

FIG. 4 is a diagrammatic representation of a  
20 second preferred embodiment of a reading configuration of the data storage and retrieval system according to the invention; and

FIG. 5 is a diagrammatic representation of a third preferred embodiment of a reading configuration  
25 of the data storage and retrieval system according to the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a three-dimensional optical memory using a fluorescent  
30 photosensitive material as the storage medium, and also a method and apparatus for the storage and retrieval of data on such three-dimensional optical memory. Preferably, the fluorescent photosensitive material is

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- a fluorescent photosensitive glass or a fluorescent photosensitive vitroc ceramic. Preferred embodiments of fluorescent photosensitive glass that can be used in the present invention are described in copending U.S.
- 5 Patent Application No. 09/123,131 filed July 27, 1998, which is incorporated herein by reference in its entirety. Preferred embodiments of fluorescent photosensitive vitroc ceramic that can be used in the present invention are described in copending U.S.
- 10 Patent Application No. 09/123,133 filed July 27, 1998, which is incorporated herein by reference in its entirety.

In accordance with a preferred embodiment of the present invention, data is written and read using

15 one or more lasers. Writing preferably is performed using a laser at a wavelength that causes a transition in the fluorescence property of the memory material. Reading preferably is performed using a laser at a wavelength that excites fluorescence in the memory

20 material. In some cases, the writing and reading -- wavelengths may be the same, and only a higher beam intensity is needed for writing, in which case one laser can be used if a one-photon process is acceptable. However, normally the writing and reading

25 wavelengths will be different, and in addition a two-photon process will be desirable to reduce the size of the volumes of the optical memory used to store individual bits, so at least two lasers will be used for writing and reading. Indeed, unless the same

30 wavelength for reading can also be used as one of the wavelengths in two-photon writing -- e.g., at a higher intensity, it may be necessary to use a third laser in a reading and writing system. Of course, in a reading system used by an end user, only one light source may

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be required to excite the memory to its fluorescence state, although a two-photon reading process, which could require two light sources, could also be used.

Preferably, the memory material is formed  
5 into a cylindrical form, as in known disk drives, which preferably is rotated by a conventional motor as is normally used in disk drives for such purposes. The laser or lasers are aimed using conventional radial or vertical scanning systems to allow, in conjunction with  
10 the rotating disk, selection of a preferred volume at coordinates  $(r, \theta, z)$ .

More specifically, information is preferably stored and recorded on the fluorescent photosensitive optical storage medium by irradiating a selected volume  
15 of the optical storage medium preferably with a coherent light beam of predetermined wavelength  $\lambda_0$ , and in one type of two-photon system the optical memory is also irradiated by a coherent light beam at a second predetermined wavelength  $\lambda_0'$ .

20 Irradiation of the volume at wavelength  $\lambda_0$  or  $\lambda_0$  and  $\lambda_0'$  causes the selected volume of fluorescent material to undergo a transition in the fluorescence properties of the optical storage medium (at the electronic level for fluorescent photosensitive glass  
25 described above and at a structural level for the fluorescent photosensitive vitroc ceramic described above) which produces a fluorescence extinction in the case of the glass described above and a fluorescence enhancement in the case of the vitroc ceramic described  
30 above. This fluorescence transition is confined to the irradiated areas.

As a result, while reading the optical memory, individually selected volumes of the fluorescent photosensitive glass that have been

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irradiated during the writing process will fluoresce less than the remainder of the glass upon being excited by a reading light beam at a predetermined excitation wavelength. In the case of fluorescent photosensitive vitrocera-  
5 mic, the specific volume that has been irradiated during writing will fluoresce more than the remainder of the vitrocera-  
mic upon being excited by a reading light beam at a predetermined excitation wavelength. Preferably, the reading light beam should  
10 be tuned to the fluorescence excitation frequency of the fluorescent photosensitive material.

Reading the optical memory is performed by identifying the difference in fluorescence intensities between a recorded volume of the medium and a non-  
15 recorded volume in the medium. These differences in fluorescence intensities can represent a sequence of code characters (e.g., 0's and 1's). For example, in the case of fluorescent photosensitive glass, extinction of fluorescence can be considered a "1"  
20 while normal fluorescence can be considered a "0", or vice versa. In the case of fluorescent photosensitive vitrocera-  
mic, enhanced fluorescence can be considered a "1" while normal fluorescence can be considered a "0", or vice versa. Of course, whatever convention is  
25 selected should be used consistently.

The data storage and retrieval system of the invention preferably uses a confocal microscope to select specific volumes of the three-dimensional optical memory during writing and reading. A confocal  
30 microscope improves depth resolution and allows a user to obtain precise depth selection in a three-dimensional structure. A confocal microscope provides a high-precision volume selection tool that prevents spherical aberrations. The confocal microscope



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operates by imaging a point light source onto an object which is located in the focal plane of the confocal microscope. Fluorescent light is emitted from the object and is directed to a photomultiplier detector through a detector pinhole. The detector pinhole is a spatial filter, which permits analysis of the light emitted only from the focal plane containing the object. This enables the confocal microscope to obtain improved spatial resolution. A computer displays the point (light emitted from the focal point) as a pixel on a screen. In order to produce a complete image, the light point is moved over the entire object, and the computer displays all of these points. The arrangement of the detector pinhole, conjugated to the illumination pinhole, ensures that only information from the focal plane reaches the detector. A confocal microscope thus has a unique ability to create images of individual sections throughout a sample with very fine detail. A confocal microscope is especially valuable in fluorescence microscopy since it almost completely eliminates stray light coming from outside the focal plane in which an object is positioned. Thus, a confocal system is able to produce fluorescence images with optimum clarity and resolution of fine details.

25           An example of a confocal microscope that can be used is the LEICA TCS NT Confocal System manufactured by the Leica Microscopy and Scientific Instruments Group, of Heerbrugg, Switzerland. The LEICA TCS NT Confocal System was used to analyze a

30   volume of under  $1 \mu\text{m}^3$  in a sample and achieved an x-y resolution of  $0.18 \mu\text{m}$  (FWHM) and a corresponding z-resolution of better than  $0.35 \mu\text{m}$  (FWHM) at  $\lambda = 488 \text{ nm}$  and a numerical aperture (N.A.) = 1.32.

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As stated above, writing in the three-dimensional optical memory according to the invention preferably is accomplished using a two-photon absorption process. Two-photon microscopy is a non-linear technique that provides improved three-dimensional resolution of a material with negligible out-of-focus photo-excitation. A two-photon process refers to the intersection of two beams at a target location to effect a change of energy level at this location. In a two-photon process, a molecule undergoes an excitation to an electronic state of higher energy by the absorption of two photons. The first photon, preferably emitted by a laser at a first predetermined wavelength, excites the molecule to a virtual state, while a second photon, preferably emitted by a laser at a second predetermined wavelength, further excites the molecule to a real excited state. The wavelengths of the two excitation beams are such that although neither beam is absorbed individually, the combination of the two wavelengths is in resonance with a molecular transition. Therefore, both beams should preferably overlap temporally and spatially for two-photon absorption to result. (See S. Hunter, F. Kiamilev, S. Esener, D.A. Parthenopoulos, P.M. Rentzepis, Applied Optics 29 (14) (1990), 2058.) The two laser beams preferably have wavelengths that will cause a transition in the fluorescence properties of the optical memory material. Upon being irradiated, the selected molecules undergo an energy level transition and data is stored on a bit-by-bit basis in these localized areas where the two photons are absorbed. In a two-photon process, irradiation of the molecules occurs only in the focused region -- neighboring bit locations are substantially unaffected.

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Two-photon absorption may also be accomplished using only one laser beam emitted from one laser, if the laser preferably rapidly emits extremely short high-energy pulses. A first photon emitted by the laser at a predetermined wavelength excites the molecule to a virtual excited state and before the molecule can decay from the virtual excited state, a second photon emitted by the laser at the same predetermined wavelength further excites the molecule to a real excited state. Upon absorption of the two photons, the optical memory will undergo a transition in its fluorescence properties. The pulse width, and the interval between pulses, of the laser should be shorter than the time in which the excited molecule undergoes excitation decay, thus allowing the second photon to further excite the molecule before it returns to its initial unexcited state. Of course, in this case, the two pulses will not overlap temporally, although they preferably overlap spatially.

In another preferred embodiment, writing in the three-dimensional optical memory is preferably accomplished with a one-photon absorption process. One-photon absorption irradiates an area using only one laser beam having a predetermined writing wavelength. The predetermined writing wavelength is a wavelength that can cause a transition in the fluorescence properties of the optical memory material. Performing a write operation using only one laser beam may result in the irradiation of molecules outside of the focused region -- the irradiated area is not as localized as with two-photon absorption. Therefore, a volume used to store information with a one-photon process may have to be larger than a volume used to store information

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with a two-photon process, possibly reducing the storage capacity of the memory.

With both one-photon and two-photon absorption processes, the irradiated volume of fluorescent material undergoes a transition (at the electronic level for the fluorescent photosensitive glass and at a structural level for the fluorescent photosensitive vitroc ceramic) which produces a fluorescence extinction in the case of the fluorescent photosensitive glass described above and a fluorescence enhancement in the case of the fluorescent photosensitive vitroc ceramic described above. Exciting the fluorescent photosensitive glass to read information will result in individually selected volumes of the fluorescent photosensitive glass fluorescing less than the remainder of the glass that have not been irradiated during writing. In the glass, the non-irradiated areas have a stronger fluorescence than the irradiated areas. This reduced fluorescence in areas exposed to the photoionizing radiation during -- writing may be the result of photoionized photosensitive rare earths inhibiting the fluorescence in that area. Exciting the fluorescent photosensitive vitroc ceramic to read information will result in an increased fluorescence at the specific volumes that have been irradiated during writing, as compared to the remainder of the vitroc ceramic that has not been irradiated during writing.

Reading information from the three-dimensional optical memory operates similarly to writing information to the three-dimensional optical memory. However, reading is preferably performed at a wavelength that excites fluorescence in the material, whereas writing is preferably performed at a wavelength

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that causes a transition in the fluorescence properties of the material. If the wavelengths are the same for writing and reading, then the same light beam generator (e.g., a laser) can preferably be used for both writing and reading in a one-photon process -- e.g., with a higher beam intensity used for writing. However, matching the writing and reading wavelengths is difficult, so an additional light beam generator or generators may be necessary for reading.

10 To read information from the optical memory, a light beam (e.g., a laser beam) tuned to the fluorescence excitation frequency of the optical memory material preferably irradiates the optical memory. In the case of an optical memory made from fluorescent  
15 photosensitive glass, the volumes not irradiated during the writing process will exhibit strong fluorescence, unlike the irradiated volumes that exhibit less or no fluorescence. In the case of an optical memory made from fluorescent photosensitive vitroceraic, the  
20 volumes irradiated during the writing process fluoresce -- more strongly than the remainder of the memory.

Data can preferably be retrieved from the three-dimensional optical memory by using a one-photon excitation process. With a one-photon excitation  
25 process, one reading light beam (e.g., a laser beam) having a predetermined reading wavelength illuminates the fluorescent photosensitive memory and causes a one-photon excitation at individually selected volumes of the optical memory. The reading light beam is  
30 preferably tuned to the fluorescence excitation frequency of the fluorescent photosensitive material.

Data can also preferably be retrieved from the three-dimensional optical memory by using a two-photon excitation process. With a two-photon process,

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two light beams (e.g., two laser beams) having predetermined reading wavelengths illuminate the fluorescent photosensitive memory and cause a two photon excitation at individually selected volumes.

- 5 The two light beams when superposed achieve fluorescence excitation of the fluorescent photosensitive material.

To store and retrieve information from the optical memory, specific volumes are preferably  
10 selected using conventional vertical and radial scanning systems and a conventional motor for the rotation of the memory medium. The memory medium preferably is cylindrical. The combination of these scanning systems and motor provides accurate focusing  
15 of a light beam on any specific volume  $(r, \theta, z)$  throughout the three-dimensional optical memory.

The fluorescent photosensitive material used in one preferred embodiment of the three-dimensional optical memory of the present invention is preferably  
20 fluorescent photosensitive glass as described in more detail in above-incorporated Application No. 09/123,131. Fluorescent photosensitive glass exhibits both fluorescent and photosensitive properties.

Generally, glass is obtained by cooling a  
25 melt in such a way that crystallization is suppressed. Glass also can be produced by the known sol-gel method.

Most glasses are oxide glasses. The structure of oxide glasses consists of a continuous network of glass-forming oxides in which long range  
30 order is missing. Glass-forming oxides such as  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{GeO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  have the strongest bonding strength among glass-forming oxides. Such glass-forming oxides are known as glass network formers. Oxides with weak bonding strength, such as

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oxides of alkali, alkaline earth, and rare earths cannot form a glass network and are known as modifiers.

Some glasses are fluorescent. Fluorescent glasses, when exposed to ultraviolet light, convert that ultraviolet light into visible light. The fluorescence of rare earth metal ions in glass was first observed in the 1880s (see W.A. Weyl, "The Fluorescence of Glasses", in "Coloured Glasses", Society of Glass Technology, Sheffield, England, 1951).

Fluorescent glasses are used in lasers, and the discovery of the lasing phenomenon gave a strong impetus to the development of rare earth activated fluorescent glasses. Various fluorescent glasses and their industrial applications are disclosed in U.S. Patents Nos. 3,549,554, 3,846,142, 4,075,120, and 4,076,541.

Some glasses are photosensitive. When photosensitive glasses are irradiated with short wave radiation such as ultraviolet radiation or X-rays, the optical properties of the glass in the irradiated areas are modified. Photosensitive glasses generally contain photosensitive elements such as copper (Cu), silver (Ag) and gold (Au). The photosensitive elements in the glass, upon exposure to the incident radiation, absorb that radiation. Upon heat treatment of the glass (typically above the annealing point of the glass), metal particles are precipitated thus changing the color of the glass in the irradiated areas. Upon cooling of the glass, the colored areas remain colored unless subsequently reheated to a high temperature.

Photosensitivity was initially observed by Dalton and described in U.S. Patents Nos. 2,326,012 and 2,422,472. Development of photosensitive glasses is described in U.S. Patent No. 2,515,937.

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In a preferred embodiment of this invention, the three-dimensional fluorescent photosensitive optical memories contain silicate or phosphate glasses which also include two or more rare earths. One or  
5 more of the rare earths imparts fluorescent properties to the glass while another of the rare earths included in the glass impart photosensitive properties to the glass.

Suitable base silicate glass compositions for  
10 use in this invention are both fluorescent and photosensitive, and comprise about 10 mole percent to about 80 mole percent  $\text{SiO}_2$ , up to about 54 mole percent  $\text{K}_2\text{O}$ , up to about 58 mole percent  $\text{Na}_2\text{O}$ , up to about 35 mole percent  $\text{Li}_2\text{O}$ , up to about 40 mole percent  $\text{BaO}$ , up  
15 to about 40 mole percent  $\text{SrO}$ , up to about 56 mole percent  $\text{CaO}$ , up to about 42 mole percent  $\text{MgO}$  and up to about 48 mole percent  $\text{ZnO}$ .

Suitable base phosphate glass compositions for use in this invention are both fluorescent and  
20 photosensitive, and comprise about 20 mole percent to about 80 mole percent  $\text{P}_2\text{O}_5$ , up to about 47 mole percent  $\text{K}_2\text{O}$ , up to about 60 mole percent  $\text{Na}_2\text{O}$ , up to about 60 mole percent  $\text{Li}_2\text{O}$ , up to about 58 mole percent  $\text{BaO}$ , up  
to about 56 mole percent  $\text{SrO}$ , up to about 56 mole  
25 percent  $\text{CaO}$ , up to about 60 mole percent  $\text{MgO}$  and up to about 64 mole percent  $\text{ZnO}$ . Additionally, yttrium (Y) may be included in amounts up to about 5 mole percent.

The fluorescent photosensitive glass used in the optical memory of the invention preferably is made  
30 by including two types of rare earths in a silicate or phosphate base glass. These two types of rare earths are (1) fluorescence-imparting rare earths (e.g., ytterbium (Yb), samarium (Sm), europium (Eu)) and (2) rare earth photosensitive agents (e.g.,



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erbium (Er), thulium (Tm), praseodymium (Pr), ytterbium (Yb), holmium (Ho), samarium (Sm), cerium (Ce), dysprosium (Dy), terbium (Tb), neodymium (Nd)). These rare earths may be incorporated in oxide form into the glass in amounts up to about 5 mole percent of the rare earth oxide.

When a specific area of the fluorescent photosensitive glass is irradiated at a wavelength sufficient to photoionize the photosensitive rare earth in the glass, fluorescence in that specific area diminishes. Areas which have not been so irradiated continue to exhibit a strong fluorescence. Without being bound by theory, it is believed that fluorescence is diminished in areas exposed to the photoionizing radiation because the resulting photoionized photosensitive rare earths inhibit the fluorescence in that area.

In another more particularly preferred embodiment, the fluorescent photosensitive material used in the three-dimensional optical memory of the invention is fluorescent photosensitive vitroceraic, as described in more detail in above-incorporated Application No. 09/123,133. Fluorescent photosensitive vitroceraic exhibits both fluorescent and photosensitive properties.

A vitroceraic is a glass matrix having fine crystals precipitated therein. Vitroceraic material is obtained by first melting a glass, such as a fluorosilicate glass, in any conventional manner. The resultant glass is then subjected to a heat treatment at a temperature above the glass transition temperature, thereby preferentially precipitating small crystals. Once the crystals are precipitated, the

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material has been transformed from glass to a vitrocera-  
mic.

Generally, when crystals are precipitated in a glass, the optical transmission is significantly  
5 reduced because the crystals cause light scattering. However, if the precipitated crystals are very small (e.g., smaller than the wavelength of incident light), and, if the difference in refractive index between the crystals and the glass matrix is also small, the loss  
10 of optical transmission due to light scattering is substantially minimized.

Crystal precipitation can be controlled with nucleation seeds which serve as catalysts for the crystal precipitation process. The efficiency of a  
15 given catalyst depends on a number of factors, including the similarity between the catalyst's own crystal structure and that of the crystal phase to be nucleated.

A vitrocera-  
mic exhibits different physical  
20 and chemical properties than the glass material from which it originates. Vitrocera-  
mics also are isotropic, flexible as to shape in which they can be formed, and their production cost is relatively low.

Some vitrocera-  
mics are fluorescent.  
25 Fluorescent materials convert incident light having a wavelength in one portion of the spectrum into light having a wavelength in a different portion of the spectrum. For example, when exposed to ultraviolet light, some fluorescent materials can convert that  
30 ultraviolet light into visible light. Some fluorescent materials can convert infrared light into visible light in a phenomenon known as up-conversion. In 1975, F. Auzel doped vitrocera-  
mics with rare earth metals. These vitrocera-  
mics converted infrared radiation into

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visible light (see F. Auzel, et al., Journal of Electrochemical Society 122(1)(1975), 101).

Some vitroceraamics are photosensitive. When photosensitive vitroceraamics are irradiated with short wavelength radiation such as ultraviolet radiation or X-rays, the optical properties of the material in the irradiated areas are modified. Photosensitive vitroceraamics generally contain photosensitive metals such as copper (Cu), silver (Ag) and gold (Au). The photosensitive metals, upon exposure to the incident radiation, absorb that radiation. Upon heat treatment, the photosensitive metal particles are precipitated in the irradiated areas and serve as nucleation seeds for subsequent crystal formation. The resultant crystals change the color of the vitroceraamic in those irradiated areas.

Photosensitive vitroceraamics have been obtained as described in U.S. Patent No. 2,651,145. This process for producing a photosensitive vitroceraamic requires that a sodium-silica base glass containing silver as a photosensitive element be exposed to ultraviolet light. The silver absorbs the incident radiation. Next, a heating process is employed to generate a photographic image by precipitating silver particles in the irradiated areas. These silver particles, in turn, provide nucleation sites for the growth of NaF crystals. The NaF crystals are large enough to scatter visible light, resulting in a white opaque image, which is opal-like in appearance.

In another embodiment of this invention, the three-dimensional fluorescent photosensitive optical memories contain fluorosilicate vitroceraamics which include one or more photosensitizing metals and one or more rare earths.

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In order to make a vitroceramic which is both fluorescent and photosensitive for use as an optical memory according to the present invention, it is first necessary to formulate a fluorosilicate base glass  
5 which also includes one or more photosensitizing metals and one or more rare earths.

Suitable fluorosilicate base glass compositions comprise about 10 mole percent to about 60 mole percent  $\text{SiO}_2$ , about 5 mole percent to about 60  
10 mole percent  $\text{PbF}_2$ , about 0.05 mole percent to about 0.3 mole percent  $\text{Sb}_2\text{O}_3$ , up to about 0.05 mole percent  $\text{CeO}_2$ , up to about 60 mole percent  $\text{CdF}_2$ , up to about 30 mole percent  $\text{GeO}_2$ , up to about 10 mole percent  $\text{TiO}_2$ , up to about 10 mole percent  $\text{ZrO}_2$ , up to about 40 mole percent  
15  $\text{Al}_2\text{O}_3$ , up to about 40 mole percent  $\text{Ga}_2\text{O}_3$  and about 10 mole percent to about 30 mole percent  $\text{Ln}_1\text{F}_3$  where  $\text{Ln}_1$  is yttrium (Y) or ytterbium (Yb).

The fluorescent photosensitive vitroceramic is made by including in the fluorosilicate base glass  
20 one or more photosensitive metals such as silver (Ag), gold (Au) and copper (Cu) and one or more rare earths such as terbium (Tb), praseodymium (Pr), dysprosium (Dy), erbium (Er), holmium (Ho), europium (Eu) and thulium (Tm). These rare earths may be incorporated  
25 into the glass in the form of  $\text{Ln}_2\text{F}_3$  (where  $\text{Ln}_2$  is the rare earth) in amounts from about 0.1 mole percent to about 5 mole percent. The photosensitive metal is incorporated in amounts of about 0.01 mole percent to about 0.5 mole percent.

30 If after the fluorosilicate base glass containing one or more rare earths and one or more photosensitizing metals is prepared, the resulting glass is then exposed to ultraviolet light in specific areas, the photosensitizing metals in those areas

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absorb the radiation. If the glass is then subjected to heat treatment at a temperature higher than the glass transition temperature thereby causing the photosensitizing metals in the irradiated areas to precipitate and become available to serve as nucleation seeds for crystallization of fine fluoride crystals. The resulting fine fluoride crystals contain a large amount of rare earth ions.

If the entire resulting vitroceramic is then exposed to an excitation radiation in order to cause the rare earth ions to fluoresce (the requisite excitation radiation is dependent on the particular rare earth ions present in the material composition), the presence of fluoride crystals containing rare earth ions can increase the fluorescence intensity of the areas subject to the first irradiation step to levels at least about 100 times the fluorescence intensity of the areas that were not subject to the first irradiation step.

The method and apparatus for the storage and retrieval of data on a three-dimensional optical memory preferably containing fluorescent photosensitive material (e.g., glass or vitroceramic) according to the present invention will now be described with reference to the preferred embodiments of FIGS. 1-5. Because of the substantially irreversible changes that take place in the optical memory according to this invention, the optical memory system as illustrated is a WORM (write-once-read-many) system. However, it may be possible upon the development of a suitable memory material to provide a memory in accordance with the invention where the changes that take place are reversible, so that a rewritable memory can be provided.

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FIG. 1 illustrates a preferred embodiment for writing information to a fluorescent photosensitive optical memory 1 using a two-photon absorption process. In the two-photon absorption process, a coherent beam generator 5 (e.g., a laser) preferably emits a coherent light beam 9 (e.g., a laser beam) having a predetermined writing wavelength  $\lambda_0$ , and the coherent light beam is preferably directed towards a confocal microscope 2. Substantially concurrently in time, a coherent beam generator 6 (e.g., a laser) preferably emits a second coherent light beam 10 preferably having a predetermined writing wavelength  $\lambda_0'$  which is directed towards confocal microscope 2. These wavelengths  $\lambda_0$ ,  $\lambda_0'$  are preferably those wavelengths that will cause a transition in the fluorescent properties of the fluorescent photosensitive material.

Confocal microscope 2, which is preferably coupled to coherent beam generators 5, 6, in conjunction with vertical scanning system 3, radial scanning system 4 and motor 7, preferably focuses the coherent light beams 9, 10 onto a selected volume 8 of fluorescent photosensitive optical memory 1. Vertical scanning system 3 and radial scanning system 4 preferably are conventional scanning systems such as are used in disk drives. Vertical scanning system 3 preferably moves confocal microscope 2 in the vertical direction along shaft 11, while radial scanning system 4 preferably moves confocal microscope 2 in the radial direction along arm 12. Also, motor 7 is preferably of the type normally used to rotate disk drives. These scanning systems allow confocal microscope 2 to position coherent light beams 9, 10 traveling through confocal microscope 2 onto any volume  $(r, \theta, z)$  of

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optical memory 1 and record information at that location.

In this preferred two-photon writing embodiment, coherent light beams 9, 10, preferably emitted from coherent beam generators 5, 6, are focused by confocal microscope 2 so that coherent light beams 9, 10 converge to irradiate a selected volume 8 at the focal point of coherent light beams 9, 10. Selected volume 8 preferably absorbs one-photon from each coherent light beam, thus resulting in a two-photon absorption that causes a transition in the fluorescence properties of optical memory 1 at selected volume 8. Coherent light beams 9, 10 preferably have wavelengths  $\lambda_0, \lambda_0'$  that cause a transition in the fluorescence properties of the optical memory material 1. Preferably, coherent light beams 9, 10 have wavelengths in the range of between about 300 nm and about 800 nm.

In another embodiment of this two-photon writing configuration, a single coherent beam generator 5 (e.g., a laser) preferably emits a coherent light beam 9 (e.g., a laser beam) preferably in short, rapid, high-energy pulses at a predetermined writing wavelength  $\lambda_0$ . Coherent light beam 9 is preferably directed towards confocal microscope 2 and is focused to irradiate a selected volume 8 at the focal point of coherent light beam 9. Wavelength  $\lambda_0$  preferably will cause a transition in the fluorescent properties of the fluorescent photosensitive material. Selected volume 8 preferably absorbs two photons from coherent light beam 9, resulting in a transition in the fluorescence properties of the optical memory 1. In this two-photon embodiment, coherent beam generator 5 preferably emits laser beams having pulse widths below about 100

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femtoseconds (fs) and a pulse repetition rate between about 75 MHz and about 150 MHz.

As depicted in the embodiment of FIG. 1, optical memory 1 preferably is a three dimensional  
5 optical memory preferably having a cylindrical shape preferably having a diameter of between 100 mm and about 150 mm, with a particularly preferred diameter of about 120 mm. A hole is preferably located along the longitudinal axis 13 of optical memory 1 and preferably  
10 has a diameter between about 10 mm and about 20 mm. The height or thickness of the optical memory 1 is preferably between about 1.2 mm and about 100 mm.

FIG. 2 illustrates another embodiment for writing information onto optical memory 1 using a one-  
15 photon absorption process. A one-photon absorption process preferably uses only one coherent light beam 9 to irradiate selected volume 8 of optical memory 1. In the one-photon absorption process, coherent beam generator 5 preferably emits a coherent light beam 9  
20 preferably having a writing wavelength  $\lambda_0$  and directs light beam 9 towards confocal microscope 2. This wavelength preferably will cause a transition in the fluorescent properties of the fluorescent photosensitive material. Preferably, this coherent  
25 light beam 9 has a wavelength in the range of between about 300 nm and about 800 nm.

Confocal microscope 2, in conjunction with vertical scanning system 3, radial scanning system 4, and motor 7, preferably focuses coherent light beam 9  
30 generated by coherent beam generator 5 onto a selected volume 8 of the fluorescent photosensitive optical memory 1. Vertical scanning system 3 preferably positions confocal microscope 2 in the vertical direction along shaft 11, radial scanning system 4



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preferably positions confocal microscope 2 in the radial direction along arm 12, and motor 7 rotates optical memory 1. The combined operation of these scanning systems 3,4 and rotating motor 7 allows  
5 confocal microscope 2 to focus coherent light beam 9 and record information at any volume  $(r, \theta, z)$  in optical memory 1, by causing a one-photon absorption at selected volume 8. This one-photon absorption causes a transition in the fluorescence properties at selected  
10 volume 8 of optical memory 1.

FIG. 3 illustrates a preferred embodiment for reading information from optical memory 1 using a one-photon excitation process. In the one-photon excitation process, reading light beam generator 14  
15 preferably emits a reading light beam 15 having wavelength  $\lambda_1$ . In a more preferred embodiment, light beam generator 14 is a coherent light beam generator emitting coherent light beam 15. Wavelength  $\lambda_1$  is preferably tuned to the fluorescence excitation  
20 frequency of the fluorescent photosensitive optical memory 1. Confocal microscope 2, in conjunction with vertical scanning system 3, radial scanning system 4, and motor 7, preferably focuses reading light beam 15 generated by reading light beam generator 14 onto a  
25 selected volume of optical memory 1. Vertical scanning system 3 preferably moves confocal microscope 2 in a vertical direction along shaft 11, radial scanning system 4 preferably moves confocal microscope 2 in a radial direction along arm 12, and motor 7 preferably  
30 rotates optical memory 1. Reading light beam 15 illuminates optical memory 1 and preferably produces a one-photon excitation at the volume selected for reading.

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Read detector 16 detects the fluorescence emission from selected volume 8. The system is calibrated to recognize a particular intensity as an extinguished or enhanced intensity as compared to surrounding volumes of optical memory 1. As discussed previously, in the case of the fluorescent photosensitive glass, extinction of fluorescence can be considered a "1" while normal fluorescence can be considered a "0", or vice versa. In the case of fluorescent photosensitive vitroc ceramic, enhanced fluorescence can be considered a "1" while normal fluorescence can be considered a "0", or vice versa.

Read detector 16 can preferably be a charge-coupled device (CCD), a photodiode, a photomultiplier tube, or other device capable of detecting fluorescence emissions.

In another embodiment of this one-photon reading configuration, the fluorescent photosensitive material of optical memory 1 is such that the reading wavelength substantially matches the writing wavelength. More specifically, the wavelength which causes transitions in the fluorescence properties of the fluorescent photosensitive material is the same as the wavelength that causes a fluorescent excitation of the material. In such a case, only one light beam generator is preferably used in a one-photon process for both writing information to and reading information from optical memory 1. Normally in such an embodiment, the beam intensity used for writing would be higher than the beam intensity used for reading.

FIG. 4 illustrates a reading embodiment using a two-photon excitation process. In a two-photon excitation process, first reading light beam generator 14 preferably emits a first reading light

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beam 15 preferably having a predetermined reading wavelength  $\lambda_1$ . Second reading light beam generator 17 preferably emits a second reading light beam 18 having a preferred predetermined reading wavelength  $\lambda_1'$ .

5 Reading light beam generators 14, 17 preferably are coherent light beam generators. The two reading light beams 15, 18 when superposed achieve fluorescence excitation of the optical memory 1. The two reading light beams 15, 18 are directed toward optical  
10 memory 1, where the two reading light beams 15, 18 converge and illuminate a selected volume to be read within optical memory 1. Confocal microscope 2, in conjunction with vertical scanning system 3, radial scanning system 4, and motor 7, preferably focuses  
15 reading light beams 15, 18 generated by reading light beam generators 14, 17 onto a selected volume 8 of optical memory 1. Vertical scanning system 3 moves confocal microscope 2 in a vertical direction along shaft 11, radial scanning system 4 moves confocal  
20 microscope in a radial direction along arm 12, and motor 7 rotates optical memory 1. This enables confocal microscope 2 to focus the two reading light beams 15, 18 onto any selected volume in optical memory 1 to read any information stored therein.

25 Read detector 16 monitors the fluorescence emission of the illuminated volume to determine if the volume is in a "1" state or a "0" state (enhanced fluorescence or fluorescence extinction) as discussed above in connection with FIG. 3.

30 In another embodiment of this two-photon reading configuration, reading light beam generator 14 (e.g., a laser) preferably emits a reading light beam 15 (e.g., a laser beam) preferably in short, rapid, high-energy pulses at a predetermined reading

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wavelength  $\lambda_1$ . Reading light beam 15 is preferably directed towards confocal microscope 2 and is focused to excite a selected volume 8 at the focal point of reading light beam 15. Selected volume 8 preferably  
5 absorbs two photons from reading light beam 15, resulting in a fluorescence excitation of optical memory 1. In this two-photon embodiment, reading light beam generator 14 preferably emits laser beams having pulse widths below about 100 femtoseconds (fs) and a  
10 pulse repetition rate between about 75 MHz and about 150 MHz.

FIG. 5 illustrates another embodiment for reading information in accordance with the invention. Reading light source 19 preferably emits a light beam  
15 20 having wavelength  $\lambda_1$  to illuminate a volumetric slice of optical memory 1, as opposed to only specific individual volumes. Preferably, reading light source 19 can illuminate an entire plane or multiple planes within optical memory 1. Reading light source 19 can  
20 preferably be a laser, a semiconductor diode laser, a mercury vapor lamp or other device capable of generating a light beam at wavelength  $\lambda_1$ , which preferably is the fluorescence excitation wavelength of the fluorescent photosensitive optical memory 1.

25 The entire illuminated band will fluoresce, except that volumes that have been written to contain information and have undergone a transition during the write process will exhibit a fluorescence extinction in the case of the fluorescent photosensitive glass  
30 optical memory or a fluorescence enhancement in the case of the fluorescent photosensitive vitroc ceramic optical memory. Read detector 16 preferably detects the fluorescence emission from the selected volume to determine if the volumes within optical memory 1 are in

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a "1" state or a "0" state. In a preferred embodiment, read detector 16 detects fluorescence extinction or fluorescence enhancement occurring in the uppermost plane or uppermost layer in the illuminated band. Any  
5 fluorescence emissions from lower planes preferably will be overpowered by the emission from the uppermost plane, so that the height of the illuminated band is not important. Reading the uppermost plane or uppermost layer from above optical memory 1 preferably  
10 avoids noise which may result from reading through other volumes that may be excited, whether by reading from the side, or by reading from above but in a plane other than the uppermost plane. Vertical scanning system 3 moves reading light source 19 in the vertical  
15 direction along shaft 11 to allow reading light source 19 to illuminate any selected volumetric slice within optical memory 1. Radial scanning system 4 preferably moves confocal microscope 2 in the radial direction along arm 12 to allow read detector 16 to detect the  
20 fluorescence emission from selected volumes within optical memory 1. In combination with the rotation of optical memory 1 by motor 7, this allows read detector 16 to monitor the fluorescence emission of any illuminated volume in optical memory 1.

25           The coherent beam generators used in the invention can preferably be any type of laser capable of emitting short, high-energy pulses. Short high-energy pulses of light minimize damage to the three-dimensional optical memory material. A pulse laser  
30 used in this invention preferably has a pulse width in the range of between about 50 fs and about 150 fs.

In a preferred embodiment, the coherent beam generators are preferably Ti:sapphire lasers preferably having an oscillating wavelength in the range of

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between about 700 nm and about 800 nm, a pulse width preferably in the range of between about 50 fs and about 150 fs, a repetition rate preferably in the range of between about 75 MHz and about 150 MHz, and a peak  
5 power preferably in the range of between about 50 kW and about 200 kW.

In another embodiment, the coherent beam generators are preferably Xenon Chloride (XeCl) lasers preferably having a wavelength of about 308 nm, or  
10 Neodymium:Yttrium-Aluminum-Garnet (Nd:YAG) laser preferably having a wavelength of about 532 nm.

In another embodiment, a two-dimensional optical memory storage device is made from fluorescent photosensitive materials. The data storage and  
15 retrieval system of this invention will increase the capacity of such a memory by reducing the size of individual areas used to store individual bits.

The present invention was tested on a three-dimensional optical memory made from fluorescent  
20 photosensitive glass doped with cerium and europium.  
-- The fluorescent photosensitive glass had the following composition:  $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-0.005 \text{ CeO}_2-0.005 \text{ Eu}_2\text{O}_3$ .

Information was written to the three-dimensional optical memory using a XeCl laser having a  
25 wavelength  $\lambda_1 = 308 \text{ nm}$  to irradiate selected volumes of the optical memory. The irradiated volumes of the fluorescent photosensitive glass experienced a fluorescence extinction. Information was read from the optical memory using a one-photon excitation process,  
30 where a second laser, an Nd:YAG laser, having a wavelength of  $\lambda_2 = 532 \text{ nm}$ , was used to illuminate the optical memory at the fluorescence excitation frequency of the fluorescent photosensitive glass. The volumes containing information exhibited a decreased

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fluorescence as opposed to the volumes that did not contain stored information.

Similarly, the present invention was tested on a three-dimensional optical memory containing  
5 fluorescent photosensitive glass, having the following composition:  $2\text{Na}_2\text{O}-(\text{Y}_{0.94}\text{Eu}_{0.05}\text{Pr}_{0.01})_2\text{O}_3-5\text{P}_2\text{O}_5$ . Information was written onto the three-dimensional optical memory using a two-photon absorption process. A tunable Ti:sapphire laser operating at wavelength  $\lambda_1 =$   
10 720 nm with 100 fs laser impulses was used to irradiate selected volumes of the memory. These irradiated volumes experienced a fluorescence extinction. Information was read from the optical memory using an Nd:YAG laser operating at wavelength  $\lambda_2 = 532$  nm to  
15 illuminate the optical memory. The volumes that have been written to exhibited a decreased fluorescence as compared to volumes that had not been written to.

The present invention was also tested on a three-dimensional optical memory made from fluorescent  
20 photosensitive vitroc ceramic doped with terbium. The optical memory had the following composition, in weight percent:  $\sim 30\text{SiO}_2-45\text{PbF}_2-14\text{Al}_2\text{O}_3-10\text{YF}_3-1\text{TbF}_3-0.05\text{Sb}_2\text{O}_3-0.01$  Ag. Information was written to and read from the optical memory using a tunable Ti:sapphire laser with  
25 100 fs laser pulses to produce a two-photon absorption of the selected volumes. To write information to the optical memory, the Ti:sapphire laser was tuned to a wavelength  $\lambda_1 = 720$  nm. The irradiated volumes of the fluorescent photosensitive vitroc ceramic experienced  
30 fluorescence enhancement. To read information, the laser was tuned to a wavelength  $\lambda_2 = 750$  nm to illuminate the optical memory at its fluorescence excitation frequency. The volumes which had been

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written to exhibited an enhanced fluorescence as compared to volumes that had not been written to.

The present invention was also tested on an optical memory containing fluorescent photosensitive vitrocera-  
5 mic, having a composition, in weight percent:  
~69SiO<sub>2</sub>-15.3Na<sub>2</sub>O-5ZnO-7Al<sub>2</sub>O<sub>3</sub>-0.25Tb<sub>4</sub>O<sub>7</sub>-0.25CeO<sub>2</sub>-0.2Sb<sub>2</sub>O<sub>3</sub>-  
0.01 Ag-2.3F-0.7 Br. Writing and reading were performed using a two-photon process. Writing was performed with a tunable Ti:sapphire laser with 100 fs  
10 laser pulses at a wavelength  $\lambda_1 = 720$  nm. The irradiated volumes experienced fluorescence enhancement. Reading was performed with a tunable Ti:sapphire laser having a wavelength  $\lambda_2 = 980$  nm. The volumes which had been written to exhibited an enhanced  
15 fluorescence as compared to volumes that had not been written to.

Thus it is seen that a data storage and retrieval system that increases the storage capacity of three-dimensional optical memories, providing a three-  
20 dimensional optical memory with greatly increased storage capacity over known optical memories has been provided. One skilled in the art will appreciate that the present invention can be practiced by other than the described embodiments, which are presented for  
25 purposes of illustration and not of limitation, and the present invention is limited only by the claims which follow.